

Coadsorption of CO and O on Ru(0001): A structural analysis by density functional theory

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Knowledge of the atomic geometry of a surface is a prerequisite for any detailed understanding of the surface's electronic structure and chemical properties. Previous studies have convincingly demonstrated that density functional theory (DFT) yields accurate surface atomic geometries and that reliable predictions concerning stable and metastable phases can be made on the basis of the calculated energetics. In the present work we use DFT to investigate the atomic structure of four ordered coadsorbate phases of carbon monoxide and oxygen on Ru(0001). All of the structures have a (2×2) periodicity with differing concentrations of CO molecules and O atoms. For two of these phases dynamical low-energy electron diffraction (LEED) intensity analyses have been performed and the agreement between our DFT- and the LEED-determined structures is found to be very good. We predict the atomic geometry of the third phase for which no structural determination based on experiments has been made to date. We also predict the stability of a new ordered mixed phase.

I. INTRODUCTION

The coadsorption system CO,O/Ru(0001) represents a well-studied model system^{1,2} for the investigation of the interaction and behavior of coadsorbed species that can give insight into physical processes that are relevant to heterogeneous catalysis³⁻⁵. Quite clearly, in order to describe and understand chemical reactions at surfaces and the surface's electronic structure, it is at first necessary to know the atomic geometry. It is only recently that the detailed atomic structure of some of the phases of CO,O on Ru(0001) have been determined, and new ones discovered. Depending on the experimental preparation, coadsorption of CO and O on Ru(0001) have been reported to form the following phases: (2×2) -(1O+1CO)^{2,6}, (2×2) -(2O+1CO)⁷, and (2×2) -(1O+2CO)⁸. In the rest of the paper we omit indicating the periodicity since for all of the coadsorption structures considered, it is the same. For the first two structures, low-energy electron diffraction (LEED) intensity analyses have been performed: In the first phase, the O atoms occupy hcp sites and the CO molecule adsorbs in the on-top site; interestingly, a tilt of the CO molecular axis of 12.6° was identified. In the second phase, a restructuring induced by CO adsorption of the O atoms of the (2×1) ⁹ phase occurs: half of the O atoms, initially occupying the hcp sites, switch to fcc sites and CO adsorbs again in the on-top site; the other half of the O atoms remain in hcp sites. For the (1O+2CO) structure, to our knowledge, there has been no LEED intensity analysis, but infrared absorption spectroscopy (IRAS) and X-ray photoelectron spectroscopy (XPS) experiments⁸ indicate that the O atoms occupy hcp sites and the CO molecules occupy on-top and fcc sites. For this structure, it was found that in order to achieve the higher coverage of CO, notably higher exposures were necessary, i.e. $\approx 10^5$ Langmuirs. In correspondence, the

sticking coefficient, which is initially close to one, drops by a factor of 60 at CO coverages greater than ≈ 0.25 . That is, initially there is a steep CO uptake curve, thereafter there is a kink and it rises only slowly with exposure.

Previous studies of the structure and stability of adsorbate phases using density-functional theory (DFT) have demonstrated that atomic geometries and stable and metastable structures can be accurately predicted (see, e.g.¹⁰⁻¹³). In the present work we perform DFT calculations¹⁴ for each of the identified phases in order to investigate, at first, the atomic structure. This work represents one of the first DFT studies of such coadsorbate systems where quantitative comparison with structures determined by LEED are made. In a subsequent publication we will report on the energetics and further details of the electronic structure. We compare our calculated atomic geometries for the (1O+1CO) and (2O+1CO) phases with the results of the LEED intensity analyses, and predict that of the to date undetermined (1O+2CO) phase. In addition, we investigated a hypothetical (3O+1CO) structure, which we predict to represent a new high density stable phase. These mixed O,CO/Ru(0001) surface structures are depicted in the top panel of Fig. 1.

II. CALCULATION METHOD

We use the generalized gradient approximation (GGA) for the exchange-correlation functional¹⁵ and the supercell approach to model the surface structures, which consists of four Ru layers. The O atoms and CO molecules are adsorbed on one side of the slab¹⁴. We use *ab initio*, fully separable pseudopotentials¹⁶ where the GGA is employed for all atoms¹⁷, and relativistic effects taken into account for the Ru atoms (using weighted spin-averaged

pseudopotentials). The positions of the C and O atoms, and the Ru atoms in the top two layers are relaxed. The energy cutoff is 40 Ry and there are three special \mathbf{k} -points in the surface Brillouin zone¹⁸.

III. O ON RU (0001)

In an earlier publication¹¹ we reported results for ordered adlayers of O on Ru(0001); some of these results will be used as reference structures for comparison¹⁹. In addition, we perform calculations for an artificial “honeycomb” (2×2) -O structure in which one O atom in the surface unit cell occupies an hcp site and the other an fcc site. The atomic geometry of the honeycomb structure is as for the $(2\text{O}+1\text{CO})$ phase, but without the CO molecules. The adsorption of oxygen on Ru(0001) under ultra high vacuum (UHV) conditions forms two ordered phases: (2×2) -O²⁰ and (2×1) -O⁹ for coverages $1/4$ and $1/2$, respectively. Recently two additional phases have been identified: (1×1) -O¹² and (2×2) -3O^{21,22} structures for coverages $\Theta=1$ and $3/4$, respectively. Formation of the latter two phases require introduction of higher concentrations of oxygen to the surface either by employing very high gas pressures of O₂ or by using “atomic oxygen” via NO₂ dissociation. In all of the ordered phases of O on Ru(0001) that form in nature, O adsorbs in the hcp site. This is the “natural” site, *i.e.* the site where also Ru would sit; it is stabilized by a lowering of the occupied DOS, following the trend that systems like to attain a chemically hard electronic structure, *i.e.* a low density at the Fermi level. Thus, essentially the same effect which stabilizes the hcp structure for Ru over the fcc structure (see e.g.²³).

IV. (1O+1CO)/RU (0001)

In the coadsorption system, $(1\text{O}+1\text{CO})$, CO adsorbs in the on-top site and O in an hcp site⁶. The structural parameters determined by LEED and DFT-GGA are given in Tab. I (compare Fig. 1). The CO bond length determined by both methods is ≈ 1.16 Å, only slightly longer than that of the free molecule which is 1.15 Å (as calculated in the present work and also as obtained experimentally, see e.g. Ref.²⁴) and only slightly shorter than that on the clean surface (≈ 1.17 Å²⁵). The LEED-determined C-Ru distance is 1.93 ± 0.06 Å (just the same as on the clean surface²⁵) and the DFT-GGA value is 1.950 Å. The position of the Ru atom to which CO is adsorbed is displaced slightly *inwards* by ≈ 0.06 Å (by LEED and DFT-GGA) relative to the top-most Ru atoms in the unit cell. As discussed in Ref.⁶, this is in apparent contrast to the behavior of CO on the clean surface where, the Ru atom is “pulled” outwards by 0.07 Å. We point out, however, that with respect to the (2×2) -O structure, the same Ru atom to which CO would adsorb is *already* displaced inwards by 0.05 Å as determined by LEED⁹ (0.043 Å by DFT-GGA¹¹), relative to the other

three surface Ru atoms. Thus CO adsorption does not actually alter the relative position of the Ru atom very much. Compared to the vertical distance between the center of mass of the first and second Ru layers of the (2×2) -O structure⁹, however, CO has induced a slight expansion, of 1.2 % as determined by LEED and 1.35 % by DFT-GGA.

The LEED intensity analysis⁶ also identified a tilt of 12.6° of the CO molecular axis in a direction between two adsorbed O atoms; it was postulated that the tilt was *static*, rather than dynamic. We investigated such a tilting of the CO axis by initially taking the identified tilt and allowing atomic relaxation. The final tilt angle was found to be 6° . The difference to the LEED result lies mainly in the lateral position of the C atom: LEED finds a very small displacement (0.05 ± 0.11 Å) while DFT-GGA obtains a larger value (0.141 Å) giving rise to a tilt of the C-O-Ru *complex* rather than just of the C-O axis. The results in any case agree to within the experimental error bars. In addition we considered tilting of the CO axis *towards* an adsorbed atom. We took the initial tilt to be that of 12.6° as determined by LEED. On relaxation of the atomic positions, we found again a tilt of $\approx 6^\circ$. On inspection of the energetics of both the tilt-geometries we found that the total energy was practically identical to the upright configuration. Thus the potential energy surface (PES) is rather flat which suggests that the CO molecule will strongly vibrate.

The corresponding electron density of the valence states for this phase is shown in Fig. 1. The oxygen atoms appear as the red, almost spherical features. Both adsorbate species can be seen to induce a redistribution of the electron density of the top-layer Ru atoms, where the C-Ru bond is clearly seen.

V. (2O+1CO)/RU (0001)

The coadsorption system $(2\text{O}+1\text{CO})$ is formed by CO adsorption onto the (2×1) -O phase. CO induces a restructuring of the O atoms such that half of them move into the fcc sites, while the other half remain in hcp sites. By doing so, CO maintains its favored on-top adsorption site. The structural parameters of this phase as determined by LEED⁷ and DFT-GGA are given in Tab. II (compare Fig. 1). It can be seen that there is good general agreement. Both LEED and DFT-GGA find a slightly shorter CO bond length (*i.e.*, of 1.15 Å and 1.155 Å, respectively) than for either CO on the clean surface (≈ 1.17 Å) or in the $(1\text{O}+1\text{CO})$ phase (≈ 1.16 Å). There is, however, a slight difference between the LEED and DFT-GGA results: The LEED-determined C-Ru bond length is *longer* in this phase than for CO on the clean surface or in the $(1\text{O}+1\text{CO})$ phase (1.98 Å compared to 1.93 Å) indicating a weaker C-metal bonding. The DFT-GGA calculations find a similar, but somewhat *shorter* C-Ru bond length (1.922 Å) than in the $(1\text{O}+1\text{CO})$ phase (1.950 Å), indicating a somewhat *stronger* bonding of CO to the metal in this phase. In a

forthcoming publication we will investigate the energetics of all the ordered mixed coadsorption phases.

The trends in the rumpling and lateral shifts of the top layer Ru atoms are agree well between LEED and DFT-GGA. Similarly to the (1O+1CO) phase discussed above, the Ru atom to which CO is bonded is displaced *inwards* relative to the other top-layer Ru atoms, by 0.09 Å (LEED) and by 0.04 Å (DFT-GGA). For the underlying O structure of the (2O+1CO) phase, which corresponds to the artificial “honey-comb” geometry described above, we point out that a similar, but *larger* difference already exists between the vertical positions of the top-layer Ru atoms; namely, the same Ru atom to which CO would bond is 0.154 Å further in towards the surface than the other Ru atoms in the surface unit cell. Therefore, relative to the position of the Ru atoms of the *honey-comb structure*, the Ru atom to which CO bonds is in fact displaced *outwards* by 0.114 Å due to CO adsorption.

While the LEED study did not report any relaxation of the second Ru layer, the DFT-GGA calculations identify small relaxations and a rumpling: The Ru atom below the hcp O atom is displaced 0.038 Å further in towards the bulk than the other three Ru atoms. These latter three Ru atoms exhibit lateral displacements of 0.013 Å radially in towards each other. The top Ru-Ru vertical displacement, using the center of mass of each layer, is 0.6 % larger than that of the honey-comb geometry, which is due to CO adsorption.

From the valence electron density (Fig. 1) it can be seen that the bonding of the hcp O atom to the metal appears to be stronger than the fcc O atom; this is what we may expect on the basis of the magnitude of the energy difference of between the hcp and fcc sites in the stable (2 × 1) structure for the same coverage¹¹.

VI. (1O+2CO)/RU (0001)

For the (1O+2CO) phase no LEED analysis exists so far. The calculated atomic geometry is depicted in Fig. 1. The CO bond length for CO in the on-top site is 1.157 Å and for CO in the fcc site the bond length is a longer 1.187 Å. For the top site, the C-Ru bond length is 1.968 Å, similar to that of the (1O+1CO) phase (and slightly longer than that in the (2O+1CO) phase, which was 1.922 Å as determined by DFT-GGA). For the fcc site the C-Ru bond length is 2.238 Å, notably longer than for CO in the on-top site; this, however, is expected due to the fact that it is *three-fold* coordinated and not one-fold. The calculations also identify small lateral displacements of 0.018 Å of the three top-layer Ru atoms in the direction towards the fcc site. Also, a rumpling of the top Ru layer of 0.129 Å occurs as indicated in Fig. 1, where again the Ru atom to which CO bonds in the on-top site is further in towards the bulk. In this case, with respect to the (2 × 2)-O structure, the Ru atom is displaced inwards by 0.086 Å (i.e., 0.129–0.043 Å). In the second Ru layer, the Ru atoms below the hcp O atoms are 0.021 Å in further towards the bulk than the other

three Ru atoms, and again these three Ru atoms display a lateral radial displacement towards each other of 0.023 Å. We hope this predicted atomic geometry can be confirmed by a LEED intensity analysis.

From the cross-section shown of the valence electron density, the bonding of the CO molecule in the fcc site can be seen to be weaker than for that of the on-top site. In the fcc site, however, CO forms three bonds with the metal surface so it is expected that they be longer and weaker.

VII. (3O+1CO)/RU (0001)

We have also studied the atomic geometry of a (3O+1CO) structure, although, to date, such a phase has not been reported to exist experimentally. Our results predict that the structure is energetically stable, although the adsorption energy is low: Starting from a (2 × 2) array of O vacancies in the full oxygen monolayer the CO adsorption energy is 0.85 eV. As mentioned above, recently it has been shown that such a (2 × 2)-3O/Ru(0001) “vacancy” or “hole” structure in fact represents a new stable phase of O on Ru(0001)^{21,22}. The stability of this phase was also indicated in our study of the thermodynamics of the O/Ru adsorption system²⁶. In order to investigate the energetics of CO adsorption into the vacant hcp site we calculated the total energy of CO at various distances above this site. We found that there is an energy barrier of ≈0.3 eV to adsorption. This implies that rather high CO pressures would be required in order to realize this structure experimentally. Providing these activation barriers can be overcome, we propose that this structure represents a new ordered (2 × 2) mixed phase of CO and O on Ru(0001). The atomic geometry is depicted in Fig. 1. Here the CO bond length is 1.181 Å, somewhat longer than for CO in the on-top site, but similar to that of CO in the fcc site for the previous structure discussed, which was 1.187 Å. In the (3O+1CO) system, there are only negligible lateral shifts of the O atoms and also only negligible rumpling of the top Ru layer (i.e., all <0.005 Å). In the second Ru layer, however, the rumpling is 0.043 Å. In this case the Ru atom directly under CO is displaced *outwards* (or upwards) relative to the other three Ru atoms. There are again only negligible lateral displacements in the second Ru layer. Due to CO adsorption, using the center of gravity of the layers, the vertical Ru-Ru distance is expanded by ≈2 % relative to the (2 × 2)-3O O-vacancy structure. Thus again, CO adsorption has induced an overall expansion of the first Ru-Ru interlayer spacing.

The valence electron density in Fig. 1 shows that there is the most disturbance of the Ru states for this structure. With respect to CO adsorption, we see four clear maxima of the electron density on the Ru atom below, while for the Ru atom that only forms bonds with O atoms, two strong maxima appear which are polarized away from the O-Ru bond. This redistribution of Ru states is seen to give rise to a build-up of electron density on top of the

Ru atoms in the top layer.

VIII. CONCLUSION

We have investigated mixed O, CO adlayers on Ru(0001). We find very good overall agreement of the atomic geometry of the (1O+1CO) and (2O+1CO) phases with those determined by LEED intensity analyses. We predict the to date undetermined structural geometry of the (1O+2CO) phase and propose the existence of a new high density phase, namely, (3O+1CO). With respect to the latter structure, adsorption of CO onto the (2×2) -3O surface in order to achieve this phase is found to be activated. This, together with the notably reduced area for CO adsorption on this surface, suggests that high CO pressures would be required to create this phase experimentally.

$(n\text{O}+m\text{CO})$ Adsorbate Phases on Ru (0001) with (2×2) Periodicity

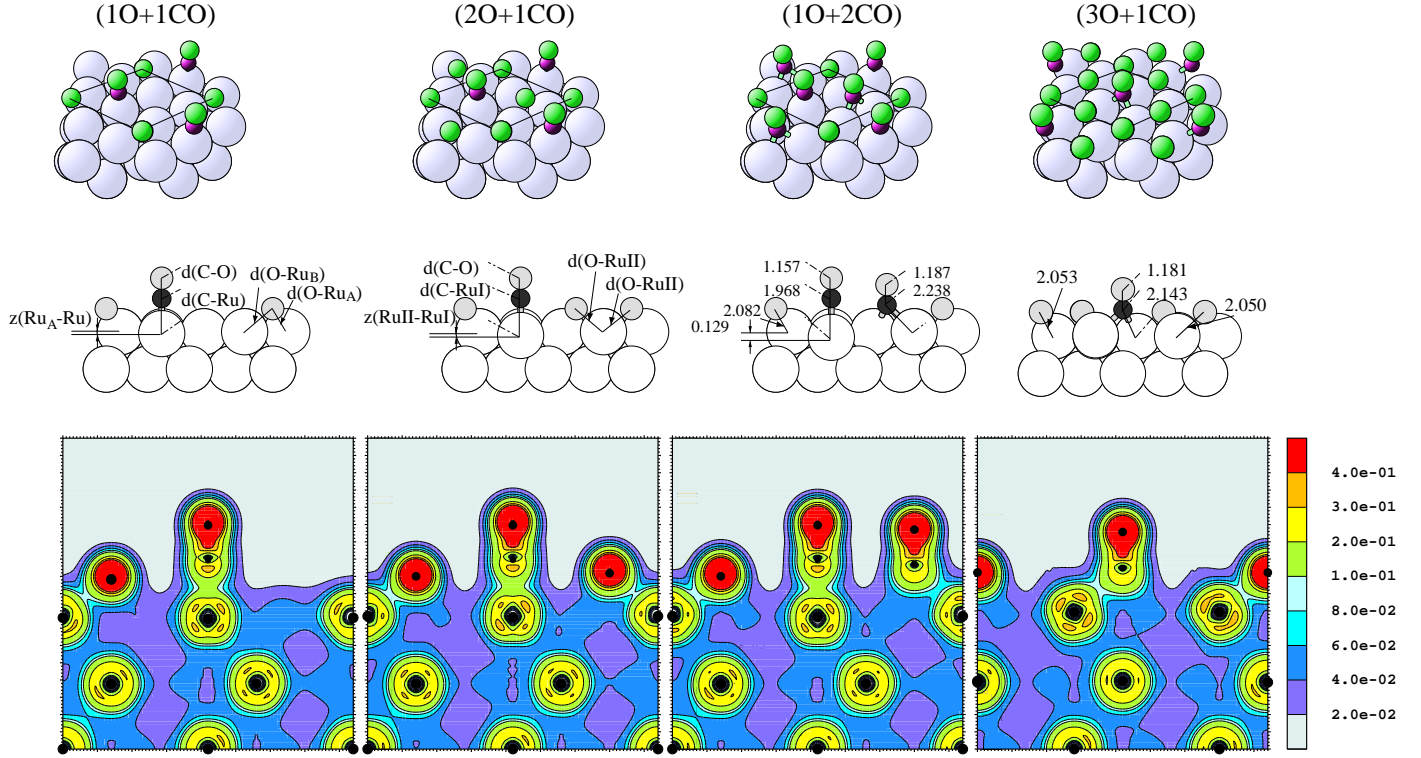


FIG. 1. Perspective and side views of the various phases of O and CO on Ru (0001). Large and small (green and red) circles represent Ru, O, and C atoms, respectively. The lower panel shows the electron density of the valence states. The contour lines are given in $e \text{ bohr}^{-3}$.

	$d(\text{C-O})$ (Å)	$d(\text{C-Ru})$ (Å)	$d(\text{O-Ru}_A)$ (Å)	$d(\text{O-Ru}_B)$ (Å)	$z(\text{Ru}_A\text{-Ru})$ (Å)	$\Delta_{\parallel}(\text{Ru}_A)$ (Å)	$\Delta_{\parallel}(\text{Ru}_B)$ (Å)
DFT-GGA	1.161	1.950	2.109	2.166	0.057	0.050	0.068
LEED	1.16 ± 0.06	1.93 ± 0.06	2.06 ± 0.08	2.09 ± 0.14	0.06 ± 0.05	0.16 ± 0.10	0.10 ± 0.10

TABLE I. Structural parameters obtained by DFT-GGA and by LEED⁶ for the (1O+1CO) phase (see Fig. 1).

	$d(\text{C-O})$ (Å)	$d(\text{C-Ru})$ (Å)	$z(\text{O(fcc)-O(hcp)})$ (Å)	$d(\text{O(hcp)-RuII})$ (Å)	$d(\text{O(fcc)-RuII})$ (Å)	$z(\text{RuII-RuI})$ (Å)	$\Delta_{\parallel}(\text{RuII})$ (Å)
DFT-GGA	1.155	1.922	0.157	2.080	2.122	0.040	0.039
LEED	1.15 ± 0.04	1.98 ± 0.08	0.19 ± 0.09	2.05 ± 0.16	2.05 ± 0.16	0.09 ± 0.02	0.08 ± 0.08

TABLE II. Structural parameters obtained by DFT-GGA and by LEED⁷ for the (2O+1CO) phase (see Fig. 1).

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